Application Note: 52127

Angle Resolved XPS for the Characterization of Self Assembled Monolayers

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Key Words

- Theta Probe
- ARXPS
- SAMs
- Surface Analysis
- XPS

The Thermo Scientific Theta Probe was used to characterize self assembled monolayers on a gold surface with ARXPS. This made it possible to determine the attachment scheme of the layers, the thickness of these layers and the way in which the concentration of material or chemical states varies within the top few nanometers of the material.

Introduction

Self assembled monolayers (SAMS) are increasingly important as a means to functionalize surfaces to control surface properties or reactivity. The length of many of the molecules used in these layers and, therefore, the thickness of the monolayers formed by them is less than the sampling depth of the XPS process. This means that the XPS technique is ideal for characterizing the layers. The additional benefits from Angle Resolved XPS are important for the determination of layer orientation and thickness.

The monolayers used in this study were a set of alkane thiols on gold, and 1-mercapto-11-undecyl-tri(ethylene glycol) on gold. Figure 1 illustrates the structure of these molecules used to produce these monolayers. Figure 2 shows the expected structures these molecules produce when interacting with a gold surface.

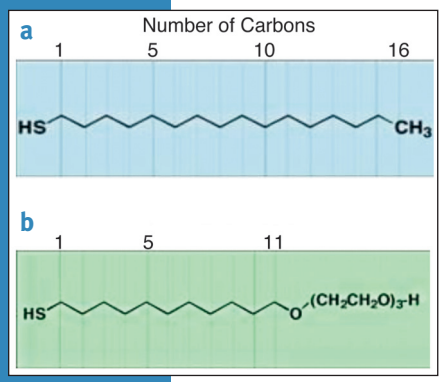

Figure 1: The structure of the molecules used in this study. a) Hexadecanethiol (an example of an alkane thiol) and b) 1-Mercapto-11-undecyl-tri(ethylene glycol).

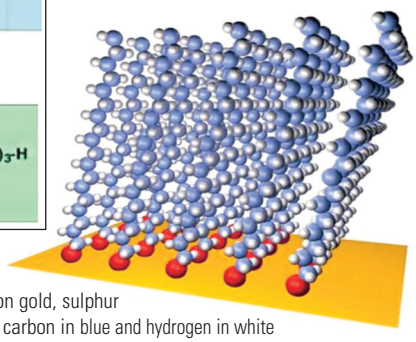

Figure 2: The structure of an alkane thiol SAM on gold, sulphur atoms are shown in red, carbon in blue and hydrogen in white

Experimental

The data were collected using the Thermo Scientific Theta Probe. Theta Probe is unique in that it can perform ARXPS measurements without tilting the sample. This has many advantages:

- Large samples can be analyzed
- Small features can be analyzed
- Thickness maps can be produced from ARXPS measurements

Measurements of the *Au4f*, *C1s*, *O1s* and *S2p* regions of the XPS spectra were made as a function of angle over a 60° range (from 20° to 80° with respect to the surface normal). These data were then used to obtain information of varying complexity from the spectra.

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Results

Relative Depth Plots

The simplest way to deal with the ARXPS data is to take the logarithm of ratio of the signals emitted at large angles and those emitted at small angles and arrange these values in order. This provides information of layer ordering. For example, Figure 3 shows the results of this type of measurement for the SAMS illustrated in Figure 1. This confirms the expected orientation of the molecules, gold as substrate bonded through sulphur above which is the hydrocarbon chain and above that is the functional group (if present, as there is in Figure 3b). While this is a very useful technique for establishing the order of layers in a sample, it contains no quantitative information.

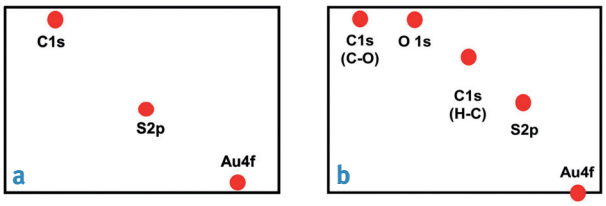

Figure 3: Relative depth plots from the two SAMS formed from the molecules shown in Figure 1

Layer Thickness

The Thermo Scientific data system, Avantage, supplied with all of our XPS instruments, contains software that will allow layer thickness to be calculated from an ARXPS data set. It can do this from samples having up to three ultra-thin layers on a substrate. If this is applied to the alkane thiol SAMs we can measure the thickness of the hydrocarbon layer as a function of the number of carbon atoms in the chain. The expected linear relationship is found, as can be seen in Figure 4.

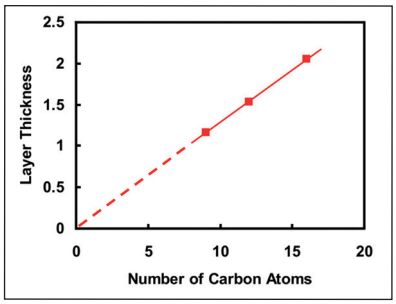

Figure 4: Layer thickness, determined by ARXPS, as a function of the number of carbon atoms in a series of alkane thiol SAMS

Generation of Depth Profiles

Mathematical methods can be applied to ARXPS data to generate non-destructive depth profiles. These are non-destructive in the sense that no material is removed during the measurement. Avantage contains algorithms that can produce such profiles; these are based on techniques involving maximum entropy. Such a profile, generated from the SAM based on the molecule shown in Figure 1b, is shown in Figure 5. In this, the chemical species appear in the correct sequence.

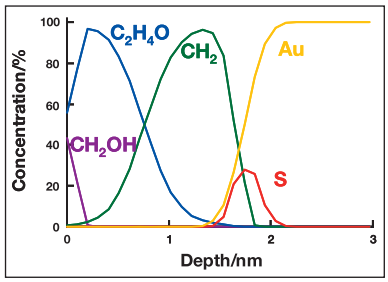

Figure 5: A non-destructive depth profile from the SAM derived from the molecule shown in Figure 1b

Summary

ARXPS is a powerful technique for the characterization of ultra-thin layers especially when it is accompanied by software containing the advanced algorithms required for the processing of the data. Using the parallel angle resolved technique available in Theta Probe the method becomes much more accessible because analysis times are decreased, small areas can be analyzed (down to 15 µm) and large samples can be analyzed (including 300 mm semiconductor wafers in the Theta 300 model). With these instruments ARXPS mapping is also possible, allowing the analyst to produce, for example, thickness maps.

Acknowledgement

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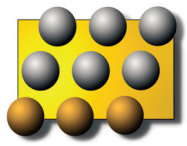

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